Methane Activation on In-Modified ZSM-5 Zeolite. H/D Hydrogen Exchange of the Alkane with Brønsted Acid Sites

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Supporting Information

**ABSTRACT:** In relation to clarifying the pathway of methane activation on In-modified zeolites, a comparative analysis of kinetics of hydrogen (H/D) exchange between methane-d₄ and Bronsted acid sites (BAS) for both the pure acid form zeolite (H-ZSM-5) and In-modified zeolites (In⁺/H-ZSM-5 and InO⁺/H-ZSM-5) has been performed. Monitoring of the kinetics has been carried out with ¹H magic-angle spinning NMR spectroscopy in situ within the temperature range of 453–568 K. While the rate of exchange on In⁺/H-ZSM-5 is 1 order of magnitude larger than that on H-ZSM-5, the exchange occurs on InO⁺/H-ZSM-5 by 2 orders of magnitude faster than that on H-ZSM-5. Significant increase of the rate and decrease of the activation energy ($E_a = 74 \pm 6$ kJ mol⁻¹) and the temperature threshold (453 K) for the reaction of the exchange on InO⁺/H-ZSM-5 compared to the rate, activation energy, and temperature threshold (543 K) for the reaction on In⁺/H-ZSM-5 ($E_a = 127 \pm 27$ kJ mol⁻¹) and H-ZSM-5 ($E_a = 118 \pm 9$ kJ mol⁻¹) have been rationalized in terms of involvement of both InO⁺ and BAS in activation of methane molecules on the zeolite. Some transient intermediate complex of methane with the zeolite InO⁺ species and BAS has been assumed to be formed within the zeolite pore. This complex is involved either in the reaction of H/D exchange with BAS of the zeolite or evolves further to offer indium methyl species.

1. INTRODUCTION

Methane is the most naturally abundant but extremely inert hydrocarbon. Therefore, its involvement in chemical transformation is a challenge for modern chemistry. Numerous attempts have been made to overcome a chemical inertness of methane with the use of heterogeneous catalysts, including metal oxides¹,² and metal-modified zeolites.³,⁴ Methane has been shown to be activated on In-modified zeolite ZSM-5 and reacted with ethylene to obtain propylene.⁵ Some conclusions on the mechanism of methane activation on In/H-ZSM-5 have been recently made.⁶ In particular, the nature of surface intermediates formed at methane interaction with indium cationic species of the zeolite has been clarified.⁷ However, the role of Bronsted acid sites (BAS) of In/H-ZSM-5 zeolite in methane activation and the formation of the surface intermediates remains unrevealed.

The hydrogen (H/D) exchange reaction between the Bronsted acid sites of solid catalysts and the alkane molecules precedes usually the alkane chemical transformation.⁸ This reaction is often used to characterize the activation of alkanes on the catalysts.⁹–²⁵ The information on the features of activation of alkane molecules can be derived by monitoring in situ the H/D exchange reaction between alkane and BAS of zeolite with ¹H MAS NMR.¹⁹,²⁶,²⁷ The application of this method to the study of H/D exchange on zeolites modified with Zn or Ga²⁷–³⁰ allowed us to establish the role of the metal centers and BAS in the activation of C₁—C₄ alkanes on these zeolites.

We have analyzed the kinetics of H/D exchange of methane with Bronsted acid sites of zeolites H-ZSM-5 modified with indium (In⁺/H-ZSM-5 and InO⁺/H-ZSM-5) and compared these kinetics with the kinetics on the pure acid form of zeolite H-ZSM-5. This approach to the study of small alkane activation on heterogeneous catalysts allowed us to establish some peculiarities of methane activation by Bronsted acid site of zeolite ZSM-5 modified by indium.

2. EXPERIMENTAL SECTION

2.1. Material Syntheses, Characterization, and Sample Preparation. The hydrogen form of zeolite ZSM-5 (H-ZSM-5) used in this work for the synthesis of the In-form zeolites was prepared from industrially produced (Tricat Zeolites) ammonium form of ZSM-5 by calcination at 773 K for 5 h. In-modified zeolite (In⁺/H-ZSM-5) was prepared by a reductive
solid-state ion-exchange reaction between indium(III) oxide and H-ZSM-5 zeolite as described previously. Approximately 30% substitution of Bronsted acid sites of parent H-ZSM-5 for indium species was reached by this procedure. 29Si magic-angle spinning (MAS) NMR analysis revealed a silicon-to-aluminum ratio of 17 for both the pure acid form and In-modified H-ZSM-5 zeolite samples. Indium content was 7.9 wt % in In/H-ZSM-5, which corresponded to indium loading of 8.0 wt % in the sample. 27Al MAS NMR spectra of the hydrated H-ZSM-5 and In/H-ZSM-5 zeolites did not show any extra framework aluminum atoms in these samples. Further, the activation of the In/H-ZSM-5 sample (100 mg) was performed in a glass tube under vacuum (10⁻³ Pa) at 673 K for 24 h. Afterward, two samples with activated In/H-ZSM-5 were prepared. Reduction of In/H-ZSM-5 in hydrogen (760 mbar) at 773 K for 30 min and further evacuation at 673 K for 2 h resulted in the sample, designated as In⁺/H-ZSM-5. The second sample, denoted as InO⁺/H-ZSM-5, was first reduced and evacuated using the method described for the previous sample. However, it was then subjected to oxygen treatment (760 mbar O₂ at 623 K for 30 min) and evacuated at 673 K for 2 h. According to X-ray photoelectron spectroscopy (XPS) and 27Al, 29Si, and 1H MAS NMR data, thus prepared In⁺/H-ZSM-5 sample showed unit cell composition In₃.₇H₁.₇Al₄.₇Al₀.₄Si₉₀.₆O₁₉₂ and contained indium in the form of In⁺ cations, whereas InO⁺ cations represented the main form of indium in InO⁺/H-ZSM-5 sample, which exhibited the unit cell composition (In₂O₄)₀.₆₆(InO⁺)₁₈H₁.₇Al₄.₇Al₀.₄Si₉₀.₆O₁₉₂.

Methane-d₄ (99% D) used in this work was purchased from Aldrich Chemical Co., Inc. Industrially produced oxygen and hydrogen gases were used without further purification.

The zeolite sample (100 mg; H-ZSM-5, In⁺/H-ZSM-5, or InO⁺/H-ZSM-5) located in axially high-symmetrical glass tube of 5.5 mm outer diameter and 10 mm length was loaded under vacuum with methane-d₄ (300 µmol g⁻¹). Afterward, the sample located in the glass tube was sealed by flame. While it was being sealed, the tube with the sample was kept in liquid nitrogen, preventing heating of the sample by the flame. The glass tube with the zeolite sample ideally fit NMR zirconia rotor (7 mm outer diameter). This allowed rotation of the sealed tube with the rate of 3000 Hz, which provided both the analysis of the reaction products in situ and monitoring the kinetics of H/D exchange with 1H MAS NMR. Samples in the sealed glass tubes were kept at room temperature prior to NMR analysis.

2.2. NMR Measurements. NMR spectra were recorded at 9.4 T on a Bruker Avance 400 spectrometer equipped with a broadband double-resonance-MAS probe. 1H MAS NMR spectra were recorded by the Hahn-echo pulse sequence (π/2−τ−π−τ−acquisition), where τ equals one rotor period (333 µs). The length of excitation π/2 pulse was 5.0 µs, and typically 16 scans were accumulated with a 10 s delay. 27Al and 29Si MAS NMR spectra were acquired under conditions similar to those described earlier. The sample temperature was controlled by a Bruker BVT-1000 variable-temperature unit. The calibration of the temperature (373–573 K) inside the rotor for kinetic measurements was performed according to the protocol described in refs 30 and 32.

Prior to acquisition of the signal at the kinetic measurements of the H/D exchange, the NMR probe with the sample was preheated for 20 min at the temperature at which the H/D exchange did not yet occur at notable rate. This temperature was 470 K for H-ZSM-5 and In⁺/H-ZSM-5 and 410 K for InO⁺/H-ZSM-5 zeolite samples. Then the temperature was rapidly increased within 3–10 min by 40–100 K to the reaction temperature and equilibrated for 4–5 min; then, the acquisition of the NMR signal started.

3. RESULTS AND DISCUSSION

The In-modified zeolite ZSM-5 (In/H-ZSM-5), prepared by reductive solid-state ion exchange between indium(III) oxide and H-ZSM-5 zeolite, contains indium species either in the form of In⁺ or InO⁺ cations. In/H-ZSM-5 treated with hydrogen at 773 K produces In⁺/H-ZSM-5 zeolite containing indium in the form of In⁺ cations. Treatment of In⁺/H-ZSM-5 with oxygen at 623 K gives the zeolite InO⁺/H-ZSM-5, in which indium exists in the form of InO⁺ cations. Both In⁺/H-ZSM-5 and InO⁺/H-ZSM-5 zeolite samples were tested in the reaction of H/D hydrogen exchange with methane-

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the signal from methane with time is indicative of H/D exchange reaction, which occurs by a transfer of protium from the acid OH group of the zeolite (BAS) to the deuterated methane and simultaneous reverse transfer of deuterium from methane-d₄ to the zeolite OH groups. Analysis of the kinetics of H/D exchange (Figure 2) shows that exchange occurs in the temperature range of 540–570 K for In⁺/H-ZSM-5, i.e., similar to the temperature range of the exchange reaction of methane with BAS of H-ZSM-5 zeolite. The activation energies of the reactions are also similar (within experimental error): 127 ± 27 and 118 ± 9 kJ mol⁻¹ for In⁺/H-ZSM-5 and H-ZSM-5, respectively. However, the rate of the exchange for In⁺/H-ZSM-5 is almost 1 order of magnitude larger than that for the exchange of methane on the pure acid form zeolite H-ZSM-5 (see Figure 3). This indicates that indium existing in the zeolite in the form of In⁺ cations accelerates the H/D exchange reaction.

For InO⁺/H-ZSM-5 zeolite, the temperature threshold of the reaction is 90 K lower than that for In⁺/H-ZSM-5 zeolite; the
exchange occurs at 450−520 K. Figure 4 shows the evolution of $^1$H MAS NMR spectrum of CD$_4$ adsorbed on InO$^+/$/H-ZSM-5 with time. The intensity of the proton signal of CH$_{n}$D$_{4-n}$ increases for the first 250 min of the reaction at 455 K, but with longer times the intensity of the signal decreases (Figures 4 and 5). A volcano shape of the kinetic curve is related to two processes occurring on the zeolite after CD$_4$ adsorption. The first process is the H/D exchange reaction of methane with BAS, and the second one is the chemical reaction of methane to afford indium methyl species CH$_3$InO. The occurrence of the latter reaction has been demonstrated recently. Although the conversion of methane into CH$_3$InO species is notable, no signal from the CH$_3$InO (−1.7 ppm) was observed in the spectra (Figure 4). This might be due to an extremely large width of this signal. The kinetic curves for methane on InO$^+/$/H-ZSM-5 (Figure 5) have been further analyzed in terms of two parallel reactions depicted in Scheme 1: the H/D exchange reaction by pathway 1 and the conversion to the indium methyl species CH$_3$InO by pathway 2 (details of kinetics scheme for deriving kinetic parameters are provided in Supporting Information). Analysis of the kinetics within a frame of Scheme 1 has shown that the rates of H/D exchange (described by rate constant $k_a$) and methane transformation to CH$_3$InO species (described by the rate constant $k_b$) are similar at the studied temperature range. The activation energies for these reactions, derived from Arrhenius plots (Figure 3), are of the similar values (74 kJ mol$^{-1}$).

The kinetic parameters derived show that while the H/D exchange occurs on In$^+/$/H-ZSM-5 1 order of magnitude faster than that on H-ZSM-5, the rate of the exchange on InO$^+/$/H-ZSM-5 is 2 orders of magnitude larger than the rate on H-ZSM-5 (see Figure 3). The activation energy of the exchange...
reaction is smaller by 50 kJ mol$^{-1}$ for InO$^+$/H-ZSM-5. These results indicate that both In$^+$ and InO$^+$ cationic species facilitate the H/D exchange reaction. However, the effect of InO$^+$ species on H/D exchange reaction is more striking, providing an essential increase of the rate and decrease of apparent activation energy and leading to the decrease of the temperature threshold for reaction proceeding by almost 90 K.

One can suggest that the promoting effect of both In$^+$ and InO$^+$ cations on the reaction of the H/D exchange is related to involvement of the cationic species by forming some transient complex with methane, which can further participate in H/D exchange with BAS of the In-modified ZSM-5 zeolites. The stronger effect of InO$^+$ species on the kinetic parameters of the exchange might indicate that the complex of methane with InO$^+$ species is more effective in terms of activation of methane molecules.

The significant acceleration of H/D exchange, coupled with the decreased activation energy on InO$^+$/H-ZSM-5 compared to that on In$^+$/H-ZSM-5 zeolite, demonstrates that the reversible cleavage and formation of the C–H(D) bonds in methane occurs with InO$^+$ species easier than with In$^+$ species. Moreover, InO$^+$ not only transfers H and D atoms between the methane and BAS of the zeolite but also participates in the chemical reaction, as has been shown before:

$$\text{CH}_4 + \text{InO}^+\text{ZO}^- \rightarrow \text{CH}_3\text{InO} + \text{ZOH}$$  \hspace{1cm} (1)

where ZO$^-$ denotes the zeolite framework.

It is reasonable to assume that the interaction of methane with InO$^+$/H-ZSM-5 gives rise to the formation of some transient complex $I$ as shown in Scheme 1. Formation of this complex implies that Al pairs should be located at appropriate distance from each other. For Si/Al = 17, statistical evaluation of Al distribution in zeolite framework predicts that the zeolite sample used in this work might contain about 30% of Al–Si–Al pairs, whereas recent experiments show that the quantity of such pairs can reach 50%.38 So the formation of complex 1 with involvement of Al–Si–Al pairs is quite possible. This complex 1 might be further involved in pathway 1, leading to the H/D exchange reaction with another acidic OH group of the zeolite. Or this complex might follow pathway 2 to form indium-methyl species CH$_3$InO. We believe that the oxygen-containing InO$^+$ species facilitates these reactions better than the same processes occurring with involvement of In$^+$ cations only.

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**Scheme 1. Possible Structure for Transient Complex I of Methane Interacting with BAS and InO$^+$ Species of InO$^+$/H-ZSM-5 Zeolite and Pathways of the Complex Evolution toward Either the H/D Exchange or the Transformation to Indium Methyl Species CH$_3$–In=O**

"H/D exchange of methane on InO$^+$/H-ZSM-5 zeolite is described by the rate constant $k_a$ and concurrent methane conversion to CH$_3$–In=O species is described by the rate constant $k_b$.\"
Thus, our experiments demonstrate a synergistic action between the exchange cations and the BAS for activating methane on In-modified zeolites. Presumably a similar mechanism is valid on other metal-modified zeolites, loaded for example with cations of Zn, Ga, or Ag.

4. CONCLUSION

We have performed a comparative analysis of the kinetics of hydrogen (H/D) exchange between methane and Bronsted acid sites for both the pure acid form zeolite (H-ZSM-5) and In-modified zeolites (In⁺/H-ZSM-5 and InO⁺/H-ZSM-5) with 1H MAS NMR spectroscopy in situ within the temperature range of 453–568 K. The analysis shows that the rate of exchange is 1 order of magnitude larger on In⁺/H-ZSM-5 and 2 orders of magnitude larger on InO⁺/H-ZSM-5 than that on H-ZSM-5. Besides dramatic increase of the rate, a notable decrease of the activation energy (E_a = 74 ± 6 kJ mol⁻¹) and the temperature threshold (453 K) for the reaction of the exchange on InO⁺/H-ZSM-5 compared to the rate, activation energy (E_a = 127 ± 27 kJ mol⁻¹), and temperature threshold (543 K) for the reaction on In⁺/H-ZSM-5 and InO⁺/H-ZSM-5 has been detected. The significant change of the kinetic parameters of the exchange for InO⁺/H-ZSM-5 is rationalized in terms of involvement of both InO⁺ species and BAS in activation of methane molecules on this In-modified zeolite. Some transient intermediate complex of methane with the zeolite InO⁺ species and BAS is assumed to be formed within the void of the zeolite pore. This complex is either involved in the reaction of H/D exchange with BAS of the zeolite or evolves further to open pore. This complex is either involved in the reaction of H/D exchange with BAS of the zeolite or evolves further to open pore. This complex is either involved in the reaction of H/D exchange with BAS of the zeolite or evolves further to open pore. This complex is either involved in the reaction of H/D exchange with BAS of the zeolite or evolves further to open pore. This complex is either involved in the reaction of H/D exchange with BAS of the zeolite or evolves further to open pore. This complex is either involved in the reaction of H/D exchange with BAS of the zeolite or evolves further to open pore. This complex is either involved in the reaction of H/D exchange with BAS of the zeolite or evolves further to open pore.

ASSOCIATED CONTENT

Supporting Information

Description of kinetics scheme for deriving kinetic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(3) Choudhary, V. R.; Kinage, A. K.; Choudhary, T. V. Low-Temperature Nonoxidative Activation of Methane over H-Gallau-
(7) Gabienko, A. A.; Arzumanov, S. S.; Moroz, I. B.; Prosvirin, I. P.; Toktarev, A. V.; Wang, W.; Stepanov, A. G. Methane Activation on In-
(18) Hua, W.; Goepert, A.; Sommer, J. H/D Exchange and Isomerization of Small Alkanes over Unpromoted and Al2O3-


NOTE ADDED AFTER ASAP PUBLICATION

This paper was published to the Web on 6/19/2014, with a minor error in the Introduction. This was fixed in the version published on 6/23/2014.